

# Laboratory studies of silicate smokes: Analog studies of circumstellar materials

Joseph A. Nuth III

NASA Goddard Space Flight Center, Greenbelt, Maryland

Susan L. Hallenbeck

NASA Headquarters, Washington, D. C.

Frans J. M. Rietmeijer

Department of Earth and Planetary Sciences, Institute of Meteoritics, University of New Mexico, Albuquerque

**Abstract.** Grains entering our solar system at the heliopause or encountered by an interstellar probe will be dominated by materials formed in carbon-rich and oxygen-rich outflows from high mass-loss-rate AGB stars with moderate contributions from novae and supernovae. Laboratory studies of the condensation and thermal evolution of silicate grains have greatly increased our understanding of grain formation processes and may provide the basis for theoretical prediction of chemical speciation and spectral evolution of grains produced in specific stellar outflows. These grains will be modified by long-term exposure to high-energy cosmic rays, thus rendering them amorphous, and will potentially be coated by one or more layers of refractory carbonaceous material. This coating results when radiation-damaged organic-rich water ices are allowed to sublime in vacuum during the transition from the interior of a dense molecular cloud to the warm interstellar medium. Measurement of the chemical compositions of large numbers of individual grains in the local interstellar medium could lead to a better understanding of the life cycle of grains in the general interstellar medium. Such measurements might also serve as a diagnostic indicator of the primary source of interstellar grains: origin in stellar outflows or in the interstellar medium itself. These measurements would be possible using an impact-ionization, time-of-flight, mass spectrometer during the cruise phase of an interstellar probe mission.

## 1. Introduction

If a scientific probe were sent to the nearest star, could useful measurements be performed during the cruise phase of the mission? In what follows we will argue that an impact-ionization, time-of-flight, mass spectrometer could obtain data that would answer several fundamental questions concerning the nature and origin of interstellar grains. In particular, such measurements would be capable of distinguishing between an origin in stellar outflows and condensation in the diffuse interstellar medium (ISM) following grain destruction in a supernova shock wave. These measurements would also distinguish between kinetically dominated circumstellar grain formation processes versus an equilibrium condensation sequence. In addition, such measurements would provide an assessment of the structure of grains in the local interstellar medium: single grains; refractory-core/organic-mantle grains; large, porous, fractal aggregates; or a combination of all possible structures.

Although a wealth of information can be extracted from measurements of the interstellar extinction curve [Mathis, 1996; Mathis *et al.*, 1977], most grains in the ISM are amorphous. Thanks to very careful measurements of the optical properties of a large number of candidate mineral phases,

many made by the Jena Group (e.g., C. Jaeger *et al.*, private communication, 1998) if crystalline materials do exist in an astrophysical environment, then these measurements could lead to the unambiguous detection of such minerals. Indeed, ISO observations have revealed the presence of some magnesium-rich minerals in certain oxygen-rich, circumstellar outflows [Waters *et al.*, 1996; Waelkins *et al.*, 1996]. Do such grains survive passage through the ISM or are they destroyed by supernova shock waves [Jones *et al.*, 1994, 1996]? Is it possible that only the crystalline order is destroyed by long exposure to the harsh interstellar environment but that the chemical composition of the grains remains mostly intact? This could explain the dominance of amorphous grains in the ISM but so might complete destruction followed by condensation. We show below that these two different scenarios should lead to very different chemical speciation within the grain population.

The compositions of grains in the ISM cannot be determined uniquely by observation of the interstellar extinction curve. Since most grains are amorphous, their observable properties are not especially sensitive to such parameters as the size and shape distribution of the individual grain components. Moreover, it is possible to remove any single component from a given ISM grain model and to substitute other components with similar spectral peaks while still obtaining a good match to the observations. There are simply too many free parameters to permit a unique solution. Inclusion of a mass spectrometer of the type already flown on cometary missions [Jessberger and

Copyright 2000 by the American Geophysical Union.

Paper number 1999JA900432.  
0148-0227/00/1999JA900432\$09.00

Kissel, 1991] would yield the first unambiguous data on the chemical compositions and mass distributions of the grain populations in the local ISM. They would also provide useful constraints to models of the interstellar extinction curve by eliminating model species that are not observed and by providing a direct measure of the relative proportions of the various grain populations. Such measurements could greatly constrain models of interstellar grains and would simultaneously constrain the origins and subsequent evolution of these grains. In what follows we will briefly review our understanding of the formation and evolution of refractory, oxide grains in the ISM in order to make clear the potential value of data obtainable using a mass spectrometer as part of the payload of an interstellar probe mission.

Refractory silicate grains are observed to form in the outflows of mass-losing, oxygen-rich stars. The spectra of these grains reveal the presence of both crystalline and amorphous magnesium silicates. Laboratory studies of the spectral evolution of annealing magnesium silicate smokes as a function of temperature and time have been used to measure the activation energy of the metamorphic transformation from chaotic condensates through to crystalline grains. These measurements allow calculation of the grain spectrum following any postulated annealing path in the circumstellar outflow: it will be shown that such calculated spectral properties are qualitatively consistent with observations. These experiments predict the formation of crystalline magnesium silicate grains, but not the formation of crystalline iron-bearing silicates. These studies are briefly discussed even though it is unlikely that any significant degree of crystallinity would survive long exposure to the cosmic rays in the ISM, since observation of specific crystalline minerals in circumstellar environments could serve as a useful diagnostic of the chemical speciation of the grains entering the ISM from stellar outflows.

We suggest that the observed spectral properties of the interstellar dust must be the result of circumstellar processes. In what follows, we will argue that the observed properties of interstellar grains are consistent with what would be expected from a simple mixture of grains formed in carbon-rich and oxygen-rich circumstellar outflows. Although only a very few experimental studies of the properties of grains formed outside circumstellar environments have been attempted, those few studies that may be marginally applicable to such processes produce materials with optical properties that are very different from those observed in the ISM. Observations of presolar grains separated from meteoritic matrix material demonstrate the widespread survival of circumstellar materials from a large number of individual sources and show few signs of the erosion predicted to occur in the ISM due to interactions with supernova shocks. For these reasons, we do not feel that it is possible, or even necessary, to produce a significant fraction of the solids observed in the ISM *in situ*.

Studies of the chemical composition of smokes nucleated from complex refractory vapors containing magnesium, iron, aluminum, silicon, hydrogen, and oxygen appear to cluster near metastable eutectics in the appropriate phase diagrams. If verified by further experimental studies, such behavior would predict the predominance of a limited number of specific chemical compositions in any given outflow, with the ratio of the number of grains of specific composition dependent on the average composition of the flow. In addition, grains from any individual outflow would be compositionally similar to grains from any other outflow unless the nucleation conditions (va-

por-composition, density, temperature) were drastically different. This observation could help to explain the remarkable degree of similarity between the spectral properties of most amorphous circumstellar silicate grains and the average oxide grain in the interstellar medium [Draine and Lee, 1984].

Each of the above topics will be discussed in more detail below in order to understand the composition and structure of silicate grains that might be encountered by an interstellar probe in the local interstellar medium or by any spacecraft that crosses the heliopause. A separate review of the composition of carbonaceous grains in the local ISM can be found elsewhere in these proceedings.

## 2. Grain Destruction in the ISM

Dust in the local interstellar medium (LISM) is a subset of material in the ISM that just happens to be in the solar neighborhood at the present epoch. This material was not present at the birth of the solar system and will not be nearby for very long provided that it does not impact a solid body orbiting the Sun, such as an Oort-cloud comet or a man-made space probe. Such material is a reasonably random, grab-bag sample of solids in the ISM. These grains will not include ices but may include coatings indicative of processed icy mantles accreted in dense clouds, now lost in the warmer, lower-density environment of the LISM. Detection of these predicted organic coatings on grains in the LISM would help to assess the rates at which materials leave dense molecular clouds and pass into lower-density environments where they might be destroyed by supernovae shocks. However, detection of a large number of coated grains would also imply that such materials could survive a very long time in such environments.

There is no doubt that supernova shock waves destroy refractory grains in the low-density ISM. This process has been observed [Seab and Shull, 1983] and is reasonably well understood [Borkowski and Dwek, 1995; Dwek *et al.*, 1996]. The major uncertainty in extrapolation of the efficiency of grain destruction in individual supernova shocks to calculate a lifetime for individual circumstellar condensates is that associated with a grain's residence time in any particular environment. Model calculations of grain lifetime [Jones *et al.*, 1994; 1996] do not explicitly deal with exchanges from the molecular cloud environment to lower-density regions such as the LISM (see models of galactic chemical evolution for additional perspectives [e.g., Clayton and Timmes, 1997]). Such models simply assume that, because the dynamic lifetime of a giant molecular cloud is  $\sim 10^7$  years, the transition from dense clouds to the warm interstellar medium also occurs on this same timescale. Observation of refractory organic coatings on only a small fraction of silicate grains in the LISM could lend validity to such an assumption.

If grains are rapidly destroyed via supernova shocks in the ISM as postulated by Jones *et al.* [1994, 1996], then the liberated refractory atoms and molecules must reform into grains on an even more rapid timescale. This assertion is based both on observations of the high depletion of refractory elements from the gas-phase of the ISM and on estimates of the relative abundance of solids needed to explain the interstellar extinction curve [e.g., O'Donnell and Mathis, 1996; Mathis *et al.*, 1977]. Unfortunately, deposition of metals and metal oxides onto the surviving fragments of the grain population that might be found behind supernova shocks will not yield spectra that are consistent with the interstellar extinction. A model based

on the presence of diatomic Mg, Fe, and Si oxide grains [Millar and Duley, 1978] was not successful in explaining the observed properties of the interstellar extinction curve. When one considers that a significant fraction of both the magnesium and iron found in the wake of a supernova shock wave would be metallic, such models are even less likely to satisfy observational constraints. Both the spectral properties of these solids and the total mass abundance in the grains (their oxygen content is very important) would be inconsistent with observations of interstellar extinction.

### 3. Prime Sources for Grains in the LISM

Carbon-rich and oxygen-rich AGB stars are natural, well-observed sources of refractory carbonaceous and oxide grains, respectively. A good first approximation to the grain population in the ISM consists of a simple mixture of grains condensed in carbon-rich and oxygen-rich AGB stars, lightly seasoned with materials produced in novae and supernovae and slowly processed through the cold of giant molecular clouds. Variation in the proportions of carbonaceous or oxide grains would naturally occur due to the local abundance of carbon- or oxygen-rich stars in individual regions. In a similar manner, the proportion of refractory core material relative to a refractory organic coating [Greenberg, 1983] or icy mantle [Sandford et al., 1997] would depend on the residence time of the grain core in various regions of a giant molecular cloud. Ice mantles would be more prevalent in the denser regions of cold cloud cores such as W33A while refractory organic mantles could be more prevalent near the cloud surface.

Oxide grains in the LISM most likely condensed in the outflows around oxygen-rich AGB stars and should signal their origin via their chemical composition as discussed below. Refractory atoms impinging onto cold grains in the wake of a supernova shock should plate out with little regard for the composition of material already stuck to the grain surface. The chemical composition of grains condensed in a circumstellar outflow could reflect some degree of thermodynamic control acting during condensation. As an example, titanium carbide grains served as the nucleation centers for the growth of graphitic grains in the atmospheres of carbon-rich AGB stars [Bernatowicz and Cowsik, 1997]. Similar calculations by Lodders and Fegley [1997, 1998] demonstrate that carbon-rich AGB outflows produce grains at locations consistent with thermodynamic predictions. We will argue below that the formation of crystalline magnesium silicate grains are also controlled to some degree by thermodynamic factors but that kinetic factors are important as well. Observations of grains in some high-mass-loss-rate oxygen-rich outflows [Waelkens et al., 1996] are consistent with predictions, based on a series of recent laboratory studies, that consider both influences.

The crystalline magnesium silicates observed by ISO and identified via their infrared spectral emission features in high-mass-loss-rate oxygen-rich circumstellar outflows [Waters et al., 1996] are not likely to remain crystalline in the ISM. Long exposure to high-energy cosmic rays would result in rapid destruction of the long range order in crystalline materials [Nuth and Hecht, 1990] and would produce a spectral signature consistent with amorphous silicates [Day, 1974, 1977; Kratschmer and Huffman, 1979]. In fact, silicate grains in the LISM would be expected to resemble GEMS, discussed elsewhere in this volume and previously discussed by Bradley [1994]. The chemical composition of GEMS displays a surprising degree of

order [Rietmeijer, 1998] especially given the highly amorphous nature of the material itself. We believe that the underlying chemical components of GEMS and, more generally, of most noncarbonaceous material in the LISM, can be traced to the conditions under which these grains formed in the outflows around oxygen-rich AGB stars.

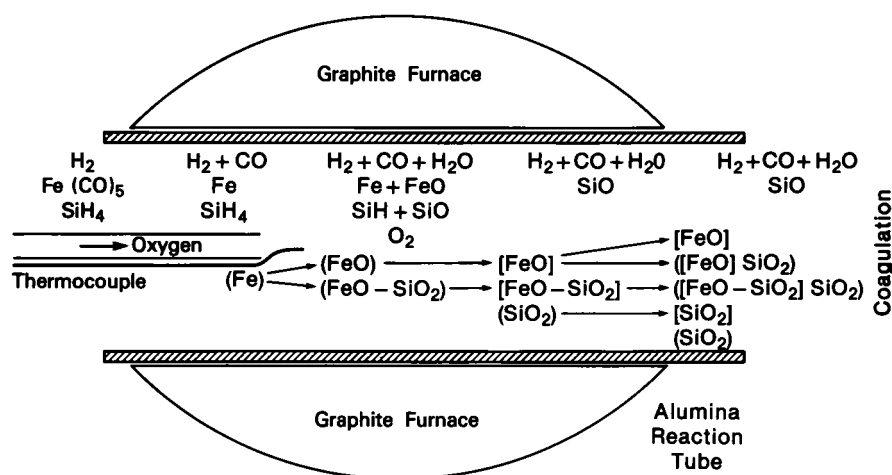
### 4. Grain Condensation in the Laboratory

We have designed and built a relatively simple combustion system in our laboratory in order to produce gram quantities of highly amorphous, refractory oxide grains [Nelson et al., 1989]. In this system silane, diluted in hydrogen or helium, can be mixed with other gaseous metal precursors (e.g., iron carbonyl, trimethyl aluminum, titanium tetrachloride) before entering an alumina-lined furnace where the incoming gas stream reacts with an oxidant (e.g., oxygen or nitrous oxide). Metals that do not have volatile precursors (e.g., magnesium, calcium, or sodium) can be added to the flow by placing a graphite boat containing the metal into the furnace. The temperature of the furnace therefore controls the vapor pressure, and relative concentration, of the metal vapor of interest. This use restricts our operating temperatures within the furnace to temperatures that produce significant quantities of the metal vapor (approximately comparable to the silane input) and often means that these experiments are run at relatively high temperature. Only one metallic species is ever placed into the furnace during a single experiment.

Total pressures during a typical run are of the order of 100 torr while the temperature of the furnace can be varied from  $\sim 500$  to  $1100$  K: temperature and pressure during any individual run are usually controlled to within  $10$  K and  $5$  torr, respectively, of the initial set points. The reactive gases are typically much less than  $10\%$  of the total flow through the system by volume: the bulk of the flow is always hydrogen and/or helium. Typical flow velocities through the furnace are of the order of  $10\text{--}20$  cm s $^{-1}$ , and a typical grain therefore spends less than a second within the furnace itself following nucleation and growth. The hot gas and fresh grains are rapidly quenched by flowing into a much larger, stainless-steel chamber at a temperature of  $\sim 300\text{--}325$  K. The grains are collected on thin aluminum or stainless steel foils in contact with the walls of the expansion chamber. The system is usually allowed to cool overnight under vacuum before the samples are collected (generally by opening the system in air).

Formation of the smokes is a stochastic, kinetically controlled process that occurs far from chemical equilibrium. Figure 1 illustrates several possible reaction pathways for the relatively simple combustion of an iron-carbonyl, silane mixture diluted in hydrogen. All such pathways appear to operate simultaneously based on AEM analysis of the grains generated in the experiment [Rietmeijer and Nuth, 1991]. Grains formed in these experiments are often fluffy, open aggregates that frequently segregate into chemically distinct regions. Figure 2 is an image of grains formed from an Fe-Al-SiO-rich gas taken using a transmission electron microscope. Typical grains are  $\sim 20\text{--}50$  nm in radius while aggregates often consist of hundreds or even thousands of individual particles, each connected to only two or three neighboring grains. The relative isolation of individual grains from the “bulk” is an important characteristic of these smokes. During thermal annealing experiments the chemical composition within individual grains tends to equilibrate and crystallize as isolated particles without regard



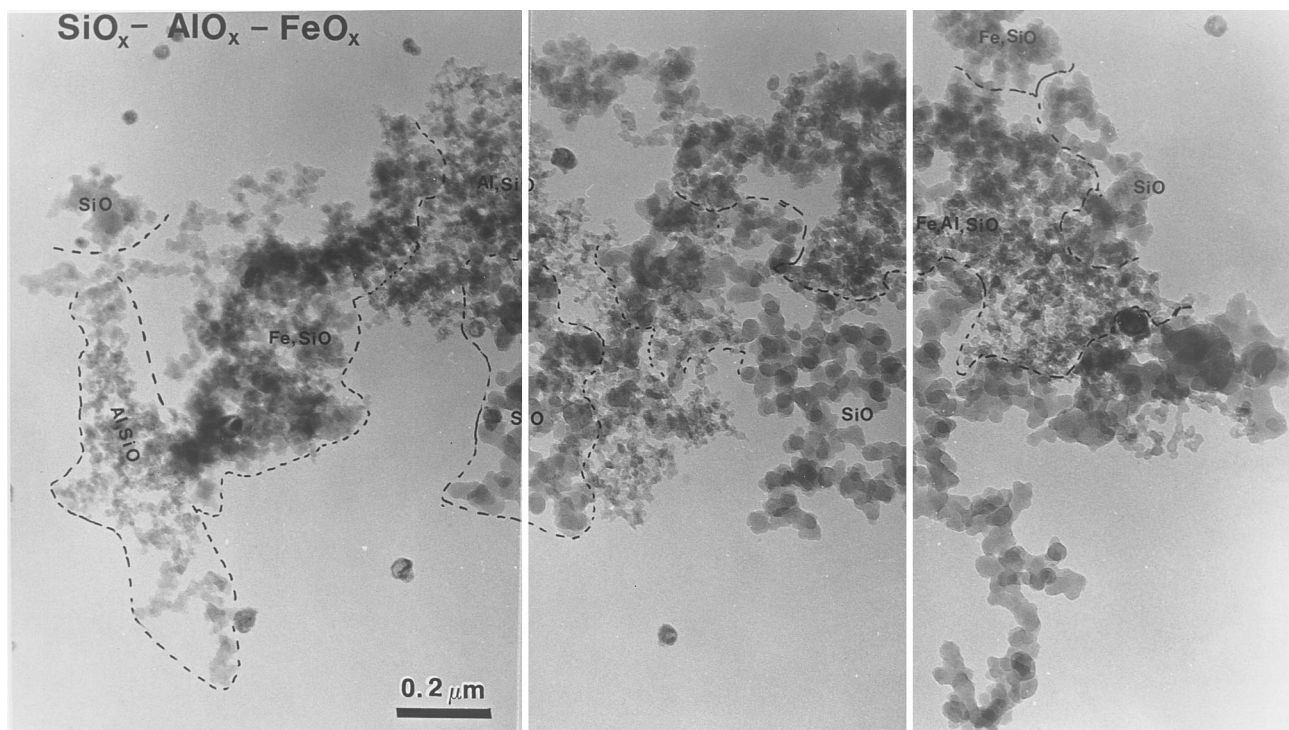


**Figure 1.** Schematic diagram of the chemical reactions that could occur in our furnace chamber during the condensation of an iron-silicate smoke based on analysis of the chemical compositions of the individual grains formed in the experiment and reasonable chemical reaction pathways that might produce such products.

for the compositions of the surrounding grains. Grains only begin to equilibrate with the bulk once significant melting occurs and the open structure collapses due to the surface tension of the liquid.

Vapor-phase nucleation and growth of refractory particles occurs on time scales of microseconds or less, under normal laboratory conditions. Such rapid growth almost always results in the formation of amorphous grains [Nuth, 1996; Nuth and Ferguson, 1993] although exceptions can occur in the vicinity of high temperature sources where annealing of the initially

amorphous condensates could produce more crystalline grains. Until very recently, there had been no reports of systematic, predictable behavior in studies of the condensation of refractory multicomponent vapors. In retrospect, there are two reasons why such behavior went unrecognized. First, most condensation experiments are carried out using pure vapors rather than binary, ternary, or even more complex mixtures such as those found in nature: multicomponent condensation experiments are quite rare. Second, even when binary or ternary systems are studied [e.g., Rietmeijer and Nuth, 1991; Rietmeijer



**Figure 2.** Transverse electromagnetic image of an iron-aluminum-silicate condensate dispersed onto a holey carbon microscope grid. Note the open structure of the aggregates and the chemical similarity of adjacent grain groupings.

*et al.*, 1986], the presence of separate phases such as tridymite, maghemite, periclase, or forsterite can more easily be attributed to incomplete mixing of vapor-phase precursors than to any systematic mechanism operating during condensation. Recognition that separate phases are actually present in the condensate requires careful, grain-by-grain analysis of the smoke rather than the use of bulk analytical techniques that merely determine the average composition of all grains present in the sample. Time consuming, grain-by-grain studies of the smokes condensed from multicomponent vapors are rarely carried out. However, recent results demonstrate that such analyses are well worth the effort.

Vapor-phase condensates produced in the laboratory at GSFC from Fe-SiO-H<sub>2</sub>-O<sub>2</sub>, Mg-SiO-H<sub>2</sub>-O<sub>2</sub>, Fe-Mg-SiO-H<sub>2</sub>-O<sub>2</sub>, Al-Fe-SiO-H<sub>2</sub>-O<sub>2</sub>, and Al-SiO-H<sub>2</sub>-O<sub>2</sub> vapors have been analyzed via transmission electron microscopy (TEM) and analytical electron microscopy (AEM) on a grain-by-grain basis in order to determine the crystal structure and chemical composition of such materials. In all cases, the chemical composition of individual grains can be predicted, based on metastable extensions of the appropriate equilibrium phase diagram. Such metastable states are familiar in a general sense to many scientists: some examples include super-cooled water droplets that have not yet frozen or super-cooled steam that has yet to condense into liquid drops. *Ostwald* [1896] observed that the phase most likely to form via condensation from a vapor will always be metastable. He hypothesized that this was due to surface energy considerations that are unimportant for bulk materials but that could dominate the thermodynamics of the very small clusters intermediate between vapor and liquid/solid.

As an example of the application of metastable eutectics to the condensation of silicate vapors, Figure 3 illustrates the equilibrium phase diagram for the FeO/Fe<sub>2</sub>O<sub>3</sub>-SiO system taken from the work of *Rietmeijer et al.* [1999b]. This diagram shows the locations of the metastable eutectics as a function of the iron/silicon oxide ratios. The metastable eutectic minima are formed by extension of stable phase boundaries (e.g., the dotted lines extending past the solid phase boundaries) beyond the point of interception with other stable phase boundaries. Figure 4 shows the equilibrium phase diagram for the Mg-SiO-H<sub>2</sub>-O<sub>2</sub> system and also indicates the locations of the predicted metastable eutectic phases (between the dotted lines). Similar predictions can be made for the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system [*Rietmeijer and Karner*, 1999] and for the more complex, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>-air vapors formed during triggered lighting experiments [*Rietmeijer et al.*, 1999a]. *Ostwald's* [1896] rule predicts that vapor-phase condensates will only form near such energetic minima. These predictions agree with our experimental results.

Most relevant to our discussion of the predicted chemical composition of grains in the LISM are the results of a single condensation experiment using Mg-Fe-SiO-H<sub>2</sub>-O<sub>2</sub> vapors. The chemical composition of individual grains formed in this experiment is shown in the ternary diagram in Figure 5. As can be seen, the compositions of the individual grains cluster at metastable eutectics along the MgO-SiO and FeO-SiO joins; however, there are no grains along the MgO-FeO join, and no grains in the interior of the diagram. The average composition of the bulk smoke as determined by low-resolution AEM [*Karner*, 1997] is shown by the large, solid "dot." The explanation for the dearth of grain compositions along the MgO-FeO join and along tie lines between Fe-SiO and Mg-SiO condensates is that in both cases such materials display no metastable

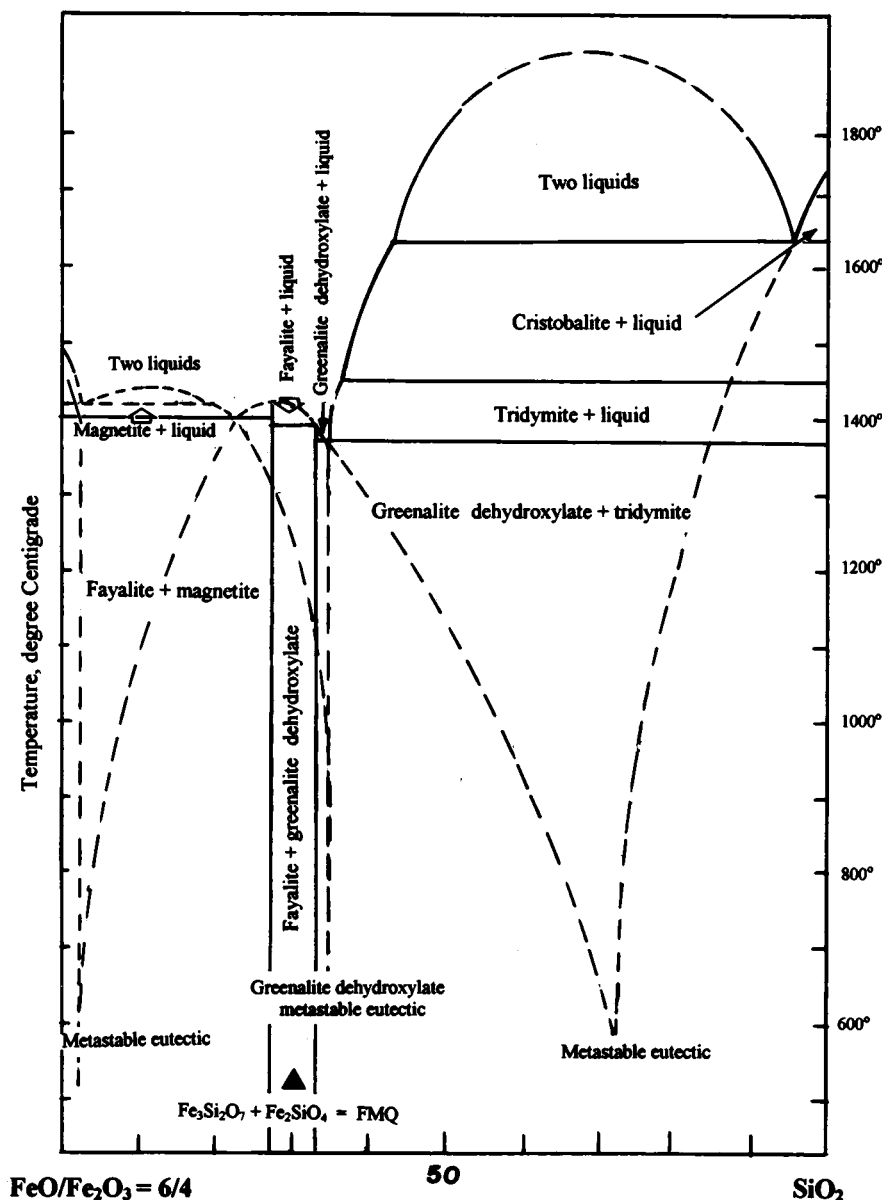
eutectic behavior along such lines. In other words, such compositions display complete solid solution across the entire range of possible compositions. With no minima in the phase diagrams, except for the pure end-member compositions, mixed grains do not condense from the vapor. If the composition of the vapor changes, our results predict that the relative abundances of the individual condensates will change but that the composition of the chemically predominate clusters will remain unchanged.

## 5. Grain Condensation in Circumstellar Outflows

If circumstellar outflows consisted only of Mg, Fe, and SiO vapors diluted in copious quantities of H<sub>2</sub>, He, and CO, the experiments and equilibrium phase diagrams cited previously predict the formation of only a handful of specific grain compositions. These compositions would include MgO, FeO/Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Mg<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>, Mg<sub>6</sub>Si<sub>8</sub>O<sub>22</sub>, Fe<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>, and Fe<sub>6</sub>Si<sub>8</sub>O<sub>22</sub>. The overall stoichiometries of stellar condensates should represent the peaks of gaussian distributions around the metastable compositions discussed above. Variations in the chemical composition of the condensing vapors would result in shifts in the relative proportions of the condensing grain types rather than in individual grains of differing composition. To first approximation increases in the concentration of Fe, Mg, or SiO in individual outflows could easily be accommodated via increased numbers of appropriate "pure" end-member oxides.

One interesting prediction of the grain formation hypothesis outlined above is that no individual, mixed (Fe-Mg-Si) oxide grains form directly from the vapor. However, since both iron-silicate and magnesium-silicate grains do form in the same outflow, and since these silicates form together with the pure oxide compositional end-members, the compositions of larger aggregates of grains formed in AGB outflows could reasonably be expected to cluster near the mean chemical composition of the outflow. Grains found in the LISM could be aggregates of individual grains formed in only one outflow or in a variety of stellar outflows, and could in the latter case contain both carbon-rich and oxygen-rich components [*Mathis*, 1996]. However, the individual sub-units of such aggregates should still reflect their origin as individual circumstellar condensates, provided that such units were never melted or significantly heated while in contact with other grains. Therefore, if it were possible to analyze the compositions of individual grains in the LISM, it should be possible to determine if the majority of the grain population were condensed in circumstellar outflows or formed in the ISM. Grains formed in outflows should show compositions consistent with the abundance peaks determined to lie around metastable eutectics, while those formed in the ISM should instead reflect the average chemical composition of refractory materials behind supernova shocks.

As an alternative to kinetically controlled refractory nucleation at metastable eutectics, similar predictions can be made based on thermochemical equilibrium condensation models [e.g., *Ebel*, this issue]. Again, analysis of individual grain compositions could also reveal a difference between grains condensed in equilibrium in a stellar outflow and those formed at relatively low temperature and density following passage of a supernova shock wave. *Ebel* [this issue] argues that thermochemical condensates should fall into approximately four groupings: refractory titanium-calcium-aluminates, magnesium silicate grains, iron-nickel-dominated metal alloy, and



**Figure 3.**  $\text{FeO}/\text{Fe}_2\text{O}_3$ - $\text{SiO}_2$  equilibrium phase diagram showing the loci of the metastable eutectic points defined by extension of the stable phase boundaries and in general agreement with the results of nonequilibrium, gas to solid, condensation experiments.

approximately everything else. Provided that these grains form independently rather than as layers, the groupings should be easily distinguishable from supernova condensates. Such groupings should also be distinguishable from metastable eutectic condensation which produces iron-silicate and aluminum silicate grains rather than the iron-nickel alloy and Ti-Ca-aluminate grains produced in equilibrium.

ISO has revealed observational evidence consistent with the kinetic model outlined above. In particular, only magnesium-rich silicates have been seen as crystalline minerals in the shells of oxygen-rich AGB stars [Waters *et al.*, 1996]. In fact, the limits on the quantity of iron that might be present in such silicates are quite severe [Tielens *et al.*, 1998]. No evidence for the presence of crystalline iron-rich silicates or for the presence of mixed iron-magnesium silicate crystals has yet been detected by ISO. In the kinetic model discussed above, one would pre-

dict the presence of pure magnesium silicate and pure iron silicate grains but would not expect to see mixed iron-magnesium silicates. In equilibrium one predicts the formation of pure magnesium silicates plus iron metal that is not detectable via infrared observations. Therefore the nondetection of pure iron silicate grains might be perceived as a problem for the kinetic model. We will show below that this is not the case. In the thermochemical model, magnesium silicates condense at temperatures near 1400 K and (given the experimental results discussed below) should all be seen as crystalline minerals. The observation of amorphous silicates in most circumstellar outflows indicates the breakdown of the equilibrium hypothesis.

Recent laboratory experiments measured the rate of spectral ( $\sim 5$ – $25 \mu\text{m}$ ) evolution of amorphous metal silicate smokes as a function of temperature for materials of various composition

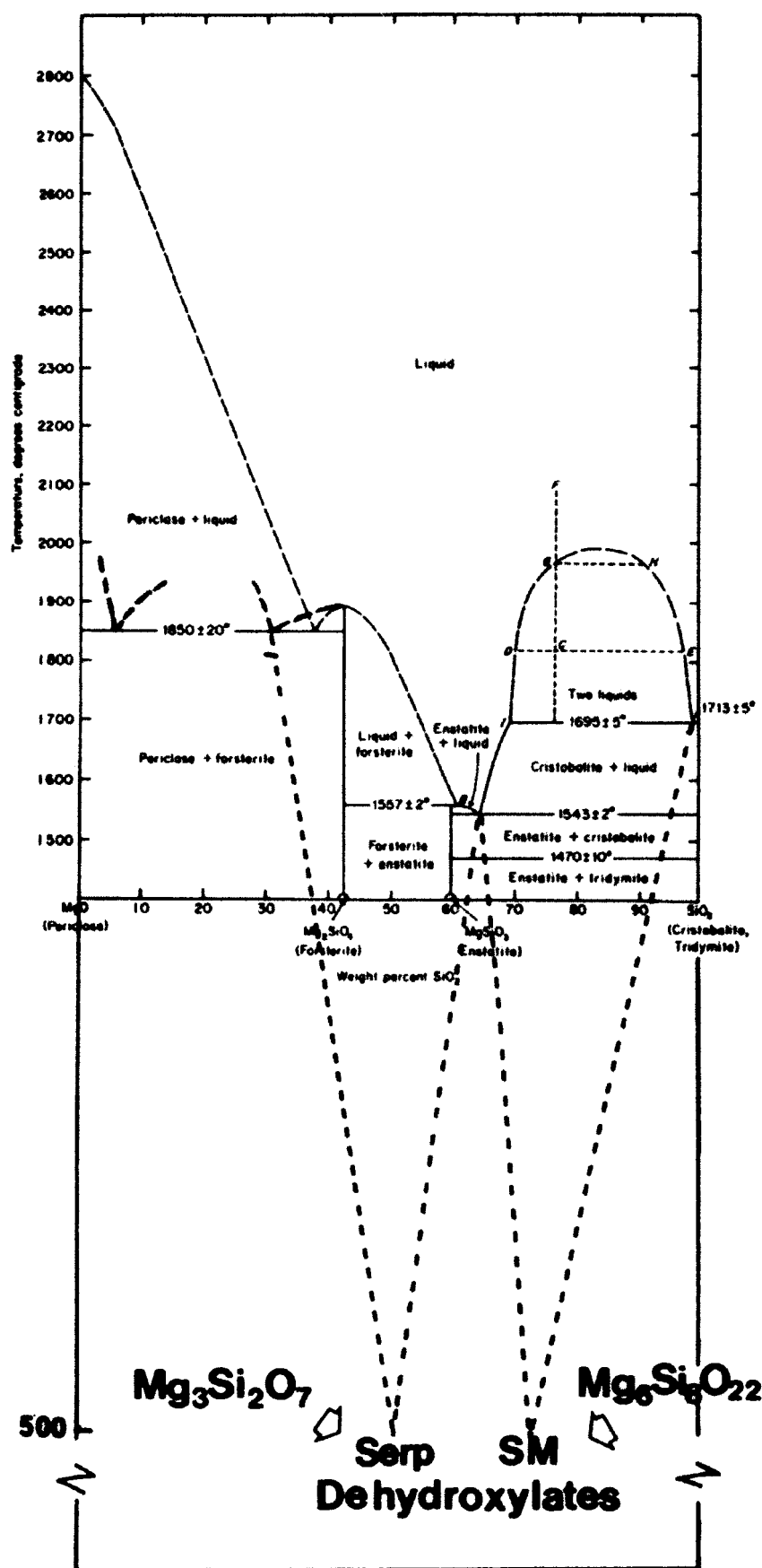
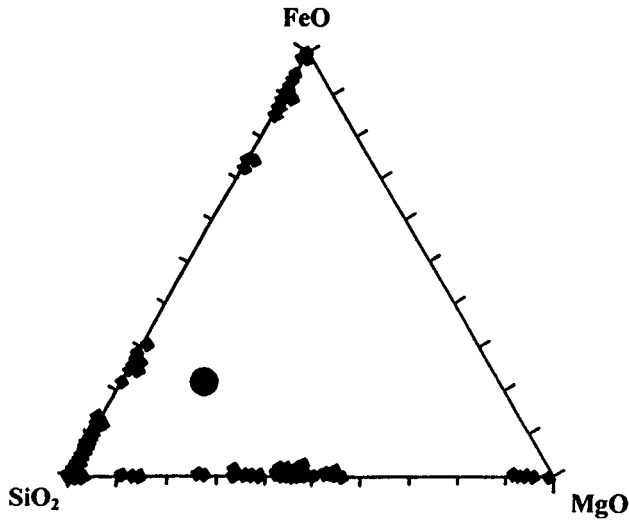


Figure 4. MgO-SiO<sub>2</sub> phase diagram showing the composition of metastable eutectics predicted at the smectite and serpentine dehydroxylate compositions.



**Figure 5.** The ternary diagram  $\text{MgO-FeO/Fe}_2\text{O}_3\text{-SiO}_2$  (oxide wt%) showing the measured compositions of individual solid grains that were formed via gas-to-solid condensation in an Fe-Mg-SiO-H<sub>2</sub>-O<sub>2</sub> vapor at  $\sim 100$  torr total pressure and at a temperature of less than 1000K. The “average bulk solid” composition (dot) should be a good proxy for the gas phase composition ( $\sim 60\%$  silica,  $\sim 20\%$  magnesia,  $20\%$  iron oxide). Condensation of this ternary vapor produced simple metal oxides plus magnesium-rich and, iron-rich silicates of compositions matching the predicted metastable eutectic compositions.

[Hallenbeck *et al.*, 1998]. These experiments demonstrated that crystalline magnesium silicates formed much more readily than did crystalline iron silicates. One very qualitative indicator used for comparison was the temperature required to observe some noticeable change in the spectrum of an amorphous smoke annealed in vacuo for one or two days. Whereas the spectra of amorphous magnesium silicate smokes changed significantly when annealed at  $\sim 1000$  K for 2 days, spectra of amorphous iron silicates did not show signs of change on this time scale unless annealed at temperatures near 1300 K. A more quantitative indicator of the degree of spectral change brought about by the thermal annealing of an amorphous magnesium silicate for a particular time at a given temperature, based on these experiments, has recently been developed [Hallenbeck *et al.*, 2000]. No similar data set is yet available for iron silicate grains, and more quantitative predictions are therefore not possible for such materials. Because we do not expect that

typical magnesium silicate grains will remain crystalline following long exposure to galactic cosmic rays we will not discuss this index further in this review.

ISO identified the presence of nearly pure, crystalline, magnesium silicate grains in high-mass-loss-rate outflows based on a series of features at wavelengths longer than 20 microns. Hallenbeck *et al.* [1998] showed that the spectra of amorphous magnesium silicates evolve more rapidly than the spectra of amorphous iron silicates, at least over the wavelength interval from 5 to 25  $\mu\text{m}$ . H. Sogawa and T. Kozasa (On the origin of crystalline silicate in circumstellar envelopes of oxygen-rich AGB stars, preprint, 1999) have shown that grains formed in higher-mass-loss-rate outflows will nucleate at higher temperatures and therefore be more readily annealed to crystallinity than will grains formed at low mass loss rates. Identification of crystalline magnesium silicates and the absence of detectable quantities of crystalline iron silicates in a particular stellar outflow is an indication that either such silicates condensed at a temperature high enough to crystallize magnesium silicate but too low to promote crystallization of iron silicate (e.g.,  $1000 \text{ K} < T < 1300 \text{ K}$ ) or that grain condensation in these stars followed an equilibrium sequence [Ebel, this issue].

The grain formation model of Kozasa and Sogawa [1997, 1998] does not preclude the formation of mixed iron-magnesium silicate grains since, in their model, silicates that eventually crystallize are formed heterogeneously on the surfaces of preexisting alumina grains. Hallenbeck *et al.* [1998] found that mixed iron-magnesium silicate smokes annealed on roughly the same timescale as did pure magnesium silicates. However, since we now know that such smokes are simply intimate mixtures of individual iron silicate and magnesium silicate grains, we must assume that the spectral changes observed in these preliminary experiments resulted from changes in only the magnesium silicate component of the mixture (the iron silicates were essentially inert during low temperature annealing). Additional experiments are needed, both to quantitatively follow the development of crystallinity in annealing iron silicates and to understand the variation of annealing rate with composition (e.g., Mg/Si).

It should be possible to deposit either an amorphous iron-metal-magnesium silicate coating or an iron-silicate-magnesium silicate coating onto an alumina surface and to monitor the time-temperature evolution of the spectral properties of the coating as a function of the iron/magnesium ratio. Such experiments would set more severe upper limits on the temperatures at which iron- and magnesium-silicate grains might have condensed heterogeneously in the outflow, based on the present observational upper limits to the amount of iron

**Table 1.** Potential Chemical Signatures of Individual Grains

Composition	
<i>Origin of Grain Cores</i>	
Stellar-equilibrium model*	Ti-Ca-AlO <sub>x</sub> , Fe-Ni alloy, Mg-silicates, other phases
Stellar-kinetic model*	Mg-SiO <sub>x</sub> , Fe-SiO <sub>x</sub> , Al-SiO <sub>x</sub> , MgO, FeO <sub>x</sub> , SiO <sub>x</sub> , AlO <sub>x</sub>
ISM condensation model*	Fe-Ni-Mg-SiO <sub>x</sub> -Ti-Ca-AlO <sub>x</sub> -C-N-H (approximately cosmic abundance)
<i>Survival of Grains in the ISM</i>	
Low rate of supernova grain destruction	any stellar grain core composition + CHON mantle
High supernova grain destruction rate	Fe-Ni-Mg-SiO <sub>x</sub> -Ti-Ca-AlO <sub>x</sub> -C-N-H (approximately cosmic abundance)

\*Core grain compositions.



contained in the crystalline grain fraction in AGB winds. If such experiments demonstrate a relatively smooth relationship between the annealing temperatures of the pure iron- and magnesium-silicate end-members as a function of iron/magnesium ratio, and the limits on the iron/magnesium ratio of crystalline grains observed by ISO remain unchanged, or become more severe, then one might reasonably question the existence of individual mixed iron-magnesium silicate grains in such outflows. Of course, the absence of such mixed silicate condensates is perfectly consistent with the results of the experiments reported in section 4.

## 6. Caveats and Conclusions

Experiments conducted in the laboratory and models constructed to emulate natural processes are all subject to the limits of their designers. The experiments discussed in sections 4 and 5 are done in much simpler and more controlled environments than those encountered in nature. Models of grain formation and destruction could contain processes that for some unknown reason, do not actually occur in nature, or might omit a mechanism that plays a pivotal role in such processes. Validation of the applicability of experiments, or models, to particular systems, must rest on the logical consequences and predictions that result from their use. Measurements of the chemical composition of oxide grains found in the local interstellar medium can be used to test the hypothesis that grain destruction occurs on a very rapid time scale in the ISM. Such measurements could also be used to support a model suggesting that most grains found in the general ISM formed in stellar outflows and to validate the experimentally based hypothesis that the nucleation of refractory vapors is controlled by metastable eutectics in multicomponent phase diagrams. This kinetic model predicts a grain population that is significantly different from the predictions of chemical equilibrium condensation and also different from condensation at low temperatures in the diffuse ISM. The potential chemical signatures of individual grains that might be measured in the LISM and the possible (model-dependent) interpretations of such data sets are shown in Table 1.

Detection of pure magnesium silicate and pure iron silicate grains, together with  $\text{MgO}$ ,  $\text{FeO}_x$ , and  $\text{SiO}_x$  end members, as the smallest individual grain components in the LISM would simultaneously validate experimental studies of refractory grain formation and the hypothesis that circumstellar outflows are the primary source of grains in the ISM. Detection of a full spectrum of mixed grain compositions from pure iron silicates through to pure magnesium silicates in grains small enough that they could not be aggregates of primary condensates, would lend support to models of heterogeneous condensation either in a circumstellar outflow or in the ISM. Detection of carbonaceous mantles on a large fraction of the grains in the LISM would call into question the relatively rapid destruction of grains by supernova shocks in low-density regions of the ISM. Such coatings are only found within molecular clouds and the lifetime of grains, once they reach such low-density environments as the LISM, is extremely short. Overall, we can conclude that careful measurement of the chemical composition of grains found in the local interstellar medium can answer some very fundamental questions concerning both the lifetime of grains in the interstellar medium and the mechanisms by which such grains form.

**Acknowledgments.** FJMR would like to thank NASA for its support under grant NAG5-4441. The ATEM work was performed at the Electron Microbeam Analysis Facility in the Department of Earth and Planetary Sciences (UNM). JAN and SLH would like to acknowledge the support of NASA's Cosmochemistry Research Program.

Janet G. Luhmann thanks Bruce Fegley and another referee for their assistance in evaluating this paper.

## References

- Bernatowicz, T. J., and R. Cowsik, Conditions in stellar outflows inferred from laboratory studies of presolar grains, in *Astrophysical Implications of the Laboratory Study of Presolar Materials*, edited by T. J. Bernatowicz and E. K. Zinner, pp. 452–474, Am. Inst. of Phys., Woodbury, N. Y., 1997.
- Borkowski, K. J., and E. Dwek, The fragmentation and vaporization of dust in grain-grain collisions, *Astrophys. J.*, **454**, 254–276, 1995.
- Bradley, J. P. Chemically anomalous, preaccretionally irradiated grains in interplanetary dust from comets, *Science*, **265**, 925–929, 1994.
- Clayton, D. D., and F. X. Timmes, Implications of presolar grains for galactic chemical evolution, in *Astrophysical Implications of the Laboratory Study of Presolar Materials*, edited by T. J. Bernatowicz and E. K. Zinner, pp. 337–264, Am. Inst. Phys., Woodbury, N. Y., 1997.
- Day, K. L., A possible identification of the 10-micron “silicate” feature, *Astrophys. J.*, **192**, L15–L17, 1974.
- Day, K. L. Irradiation of magnesium silicates with MeV protons, *Mon. Not. R. Astron. Soc.*, **178**, 49–52, 1977.
- Draine, B. T., and H. M. Lee, Optical properties of interstellar graphite and silicate grains, *Astrophys. J.*, **285**, 89–108, 1984.
- Dwek, E., S. M. Foster, and O. Vancura, Cooling, sputtering, and infrared emission from dust grains in fast nonradiative shocks, *Astrophys. J.*, **457**, 244–252, 1996.
- Ebel, D. Variations on solar condensation: Sources of interstellar dust nuclei, *J. Geophys. Res.*, this issue.
- Greenberg, J. M., The largest molecules in space: Interstellar dust, in *Cosmochemistry and the Origin of Life*, edited by C. Ponnemperuma, pp. 71–112, D. Reidel, Norwell, Mass., 1983.
- Hallenbeck, S. L., J. A. Nuth, and P. L. Daukantus, Mid-infrared spectral evolution of amorphous magnesium silicate smokes annealed in vacuum: Comparison to cometary spectra, *Icarus*, **131**, 198–209, 1998.
- Hallenbeck, S. L., J. A. Nuth, and R. N. Nelson, Evolving optical properties of annealing silicate grains: From amorphous condensate to crystalline mineral, *Astrophys. J.*, in press, 2000.
- Jessberger, E. K., and J. Kissel, Chemical properties of cometary dust and a note on carbon isotopes, in *Comets in the Post-Halley Era*, edited by R. L. Newburn, M. Neugebauer, and J. Rahe, pp. 1075–1092, Kluwer, Norwell, Mass, 1991.
- Jones, A. P., A. G. G. M. Tielens, D. J. Hollenbach, and C. F. McKee, Grain destruction in shocks in the interstellar medium, *Astrophys. J.*, **433**, 797–810, 1994.
- Jones, A. P., A. G. G. M. Tielens, and D. J. Hollenbach, Grain shattering in shocks: The interstellar grain size distribution, *Astrophys. J.*, **469**, 740–764, 1996.
- Karner, J. M., Mineralogy, morphology and chemistry of vapor-condensed silicate dust analogs, M.S. thesis, 148 pp., Univ. of N. M., Albuquerque, 1997.
- Kozasa, T., and H. Sogawa, Formation of dust grains in circumstellar envelopes of oxygen-rich AGB stars, *Astrophys. Space Sci.*, **251**, 165–170, 1997.
- Kozasa, T., and H. Sogawa, Formation of  $\text{Al}_2\text{O}_3$  grains and the 13-micron feature in circumstellar envelopes of oxygen-rich AGB stars, *Astrophys. Space Sci.*, **255**, 437–443, 1998.
- Kratschmer, W., and D. R. Huffman, Infrared extinction of heavy ion irradiated and amorphous olivine, with applications to interstellar dust, *Astrophys. Space Sci.*, **61**, 195–203, 1979.
- Lodders, K., and B. Fegley, Condensation chemistry of carbon stars, in *Astrophysical Implications of the Laboratory Study of Presolar Materials*, edited by T. J. Bernatowicz and E. K. Zinner, pp. 391–423, Am. Inst. of Phys., Woodbury, N. Y., 1997.
- Lodders, K., and B. Fegley, Presolar silicon carbide grains and their parent stars, *MAPS*, **33**, 871–880, 1998.
- Mathis, J. S. Dust models with tight abundance constraints, *Astrophys. J.*, **472**, 643–655, 1996.
- Mathis, J. S., W. Rumpl, and K. H. Nordsieck, The size distribution of interstellar grains, *Astrophys. J.*, **217**, 425–433, 1977.

- Millar, T. J., and W. W. Duley, Diatomic oxide interstellar grains, *Mon. Not. R. Astron. Soc.*, **183**, 177–185, 1978.
- Nelson, R. N., M. H. Thiemens, J. Nuth, and B. Donn, Oxygen isotopic fractionation in the condensation of refractory smokes, in *Proceedings of 19th Lunar and Planetary Science Conference*, edited by G. Ryder and V. Sharpton, pp. 559–563, Cambridge Univ. Press, New York, 1989.
- Nuth, J. A., Grain formation and metamorphism, in *The Cosmic Dust Connection*, edited by J. M. Greenberg, pp. 205–221, Kluwer Acad., Norwell, Mass., 1996.
- Nuth, J. A., and F. Ferguson, Nucleation of solids from the gas phase, *Ceramic Trans.*, **30**, 23–34, 1993.
- Nuth, J. A., and J. H. Hecht, Signatures of aging silicate dust, *Astrophys. Space Sci.*, **163**, 79–94, 1990.
- O'Donnell, J. Z., and J. S. Mathis, Dust grain size distributions and the abundance of refractory elements in the diffuse interstellar medium, *Astrophys. J.*, **479**, 806–817, 1997.
- Ostwald, W., *Lehrbuch der Allgemeinen Chemie*, vol 2, p. 2, W. Engelmann, Leipzig, Germany 1896.
- Rietmeijer, F. J. M. Interplanetary dust particles, in *Planetary Materials*, *Rev. Mineral.*, vol. 36, edited by J. J. Papike and P. H. Ribbe, chap. 2, Mineral. Soc. of Am., Washington, D. C. 1998.
- Rietmeijer, F. J. M., and J. M. Karner, Metastable gas to solid condensation in the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system, *J. Chem. Phys.*, **110**, 4554–4558, 1999.
- Rietmeijer, F. J. M., and J. A. Nuth, Tridymite and maghemite formation in an Fe-SiO smoke, *Proc. Lunar Planet. Sci. Conf. 21st*, 591–599, 1991.
- Rietmeijer, F. J. M., J. A. Nuth, and I. D. R. Mackinnon, Analytical electron microscopy of Mg-SiO smokes: A comparison with infrared and XRD studies, *Icarus*, **66**, 211–222, 1986.
- Rietmeijer F. J. M., J. M. Karner, J. A. Nuth III, and P. J. Wasilewski, Nanoscale phase equilibrium in a triggered lightning strike experiment, *Eur. J. Mineral.*, **11**, 181–186, 1999a.
- Rietmeijer, F. J. M., J. A. Nuth, and J. M. Karner, Metastable eutectic, gas to solid, condensation in the  $\text{FeO}$ - $\text{Fe}_2\text{O}_3$ - $\text{SiO}_2$  system, *Phys. Chem. Chem. Phys.*, **1**, 1511–1516, 1999b.
- Sandford, S. A., L. A. Allamandola, and M. P. Bernstein, The composition and ultraviolet and thermal processing of interstellar ices, in *From Stardust to Planetesimals*, edited by Y. J. Pendleton, and A. G. G. M. Tielens, pp. 201–213, Astron. Soc. of the Pac., San Francisco, Calif., 1997.
- Seab, C. G., and J. M. Shull, Shock processing of interstellar grains, *Astrophys. J.*, **275**, 652–660, 1983.
- Tielens, A. G. G. M., L. B. F. M. Waters, F. J. Molster, and K. Justtanont, Circumstellar silicate mineralogy, *Astrophys. Space Sci.*, **255**, 415–426, 1998.
- Waelkens, C., et al., SWS observations of young main-sequence stars with dusty circumstellar disks, *Astron. Astrophys.*, **315**, L245–L248, 1996.
- Waters, L. B. F. M., et al., Mineralogy of oxygen-rich dust shells, *Astron. Astrophys.*, **315**, L361–L364, 1996.
- S. L. Hallenbeck, Code SR, NASA Headquarters, Washington, DC 20546.
- J. A. Nuth III, NASA Goddard Space Flight Center, Greenbelt, MD 20771. (nuth@gsfc.nasa.gov)
- F. J. M. Rietmeijer, Department of Earth and Planetary Sciences, Institute of Meteoritics, University of New Mexico, Albuquerque, NM 85131.

(Received February 16, 1999; revised July 15, 1999; accepted September 21, 1999.)